Thaxylon #2

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Bescheinigung | Certificate | Attestation

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The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. | Patent application No. | Demande de brevet n°

00000003.4

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
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Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation

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Anmelder:
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Titre de l'invention:
Negative working heat-sensitive printing plate for on-press development

In Anspruch genommene Prioriät(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

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See for original title of the application page 1 of the description

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[DESCRIPTION]

FIELD OF THE INVENTION

The present invention relates to hydrophobic thermoplastic polymer particles, prepared by a specific method, and to the use of said hyrophobic polymer particles in a negative working thermal plate, which has been made sensitive to infrared radiation, for on-press development.

More specifically the present invention is related to a lithographic printing plate showing an improved chemical resistance and lithographic performance, and, more particularly, a higher runlength, a broader lithographic latitude and a better scratch resistance.

BACKGROUND OF THE INVENTION

Lithographic printing plates making use of polymer binders containing nitrogen atoms have been described in various patent applications, as being particularly suitable for use in order to increase the chemical resistance or print durability.

Toyo Gosei Kogyo KK e.g. in the Japanese patent application JP-A 07-036186 makes use of polymers with heterocyclic ring residues containing nitrogen and copolymers of acrylonitrile-butylacrylate-methyl methacrylate and triallyl isocyanurate. Toyo Gosei makes use of photosensitive vinyl acetate emulsion copolymers in combination with an hydrophilic binder, i.e. polyvinyl alcohol. In this application the photsensitive resin compositions are used for an emulsion screen printing plate.

Kodak Polychrome Graphics GMBH, in the PCT patent application filing WO 99/64930, discloses offset printing plates having a high durability. Said plates are composed of a suitable support coated with a positive- or negative-working, or electrophotographic-working radiation-sensitive composition containing an alkali soluble/insolu-

ble thermoplastic polymer that is incorporated into the compostion, making use of a solvent in which both the radiation-sensitive polymer and the thermoplastic polymer are soluble and, if required, a second solvent, less volatile than the first solvent, wherein the radiation-sensitive polymer is soluble but wherein the thermoplastic polymer is insoluble. Upon drying the photosensitive layer contains homogeneously distributed polymer particles, providing improved printing durability for the resulting exposed and developed plate. No significant coalescence of particles occurs during imaging. Moreover the said photosensitive layer contains a solvent for the employed thermoplastic polymer. Thermoplastics useful in the process are e.g. acrylonitrile-styrene polymers. Just as in the present application styrene-acrylonitrile copolymers were most preferable.

Acidic vinyl copolymers containing acrylonitrile in combination with triazines as a photopolymerization initiator have been described by Mitsubishi Chemical Industries in JP-A 11-249298. Konica, in JP-A 10-207056, makes use of acrylonitrile-benzyl methacrylate-4-hydroxyphenyl-methacrylate-methyl-methacrylate copolymers in order to prepare a lithographic printing plate with improved sensitivity, cleaner resistance and writability. A similar copolymer has been used by Konishiroku Photo Industries in JP-A 08-220766. Okamoto Kagaku Kogyo, in JP-A 05-088369, makes use of alkali-soluble copolymers of N-(4-hydroxyphenyl)maleimide, acrylonitrile, and mono(2-methacryloxyethyl)hexahydrophthalate. The corresponding plates wherein said copolymers are present, show a high photosensitivity, a wide development latitude, and good printing durability, even when using UV-inks. Thus, an anodized aluminum substrate was coated with a component containing naphthoquinon(1,2)-diazido-5-sulfonic acid ester of acetone-pyrogallol resin and acrylonitrile copolymer in order to give a presensitized lithographic plate.

Konica further describes photosensitive compositions comprising naphtoquinone diazide sulphonates and phenolic resins having a good resistance towards cleaners and oils. In JP-A's 63-183441 and 10-207056 Konica makes use of a N-(4-hydroxyphenyl)acrylamide-acrylonitrile-ethyl acrylate-methyl methacrylate copolymer binder.

In JP-A 63-066558 a similar polymer is used in a photosensitive composition containing o-quinone diazide compounds. In JP-A 10-207056 Konica describes a composition comprising (A) a compound generating an acid or a radical under irradiation of light, activated radiation or electron beams and (B) a polymer containing at least one monomer unit (a) with a dipole moment of at least 3.0 D and at least one monomer unit (b) with a dipole moment of less than 3.0 D and having Y = 1.800-2.300 (wherein Y is based on an equation, regarding the dipole moment of the monomers and the molar ratio of the monomers, as specified by the author. In JP-A 04-062556 Konica describes a nitrogen-containing polymer in a chemically resistant positive-working resist for presensitized lithographic plates.

Otherwise in JP-A 59-002045 DuPont de Nemours describes the solvent resistance of flexographic plates prepared by making use of a photosensitive elastomer composition containing an acrylonitrile-butadiene copolymer type resin.

A polymer having onium group containing structural components containing one or more onium group(s) is further used in a positive-working presensitized lithographic plate, as disclosed by Fuji in JP-A 10-301262. The lithographic plate shows good performance in erasure of unnecessary image portions, low residual color stain, and high printing durability as well as chemical resistance. In another patent application by Fuji N-containing polymers like Acrylonitrile-N-(p-Aminosulfonylphenyl)-methacrylamide-ethyl methacrylate copolymers are used. The positive-working photosensitive composition for the manufacture of a lithographic plate comprises a polymer with a sulfonamido-group, an alkali-soluble novolak and a positive-working photosensitive compound.

For use of polymer binders in an application such as a negative working lithographic printing plate, improvement of chemical resistance and lithographic performance, and, more particularly, provision of a higher runlength, a broader lithographic latitude and a better scratch resistance, is highly desired as it remains an ever lasting demand.

OBJECTS OF THE INVENTION

It is an object of the present invention to provide a negative working lithographic printing plate material, wherein said printing plate material shows an improved chemical resistance and lithographic performance, and, in particular, a higher runlength, a lithographic latitude and scratch resistance.

It is a further object to avoid environmentally unfriendly measures in the manufacturing of the printing plate, more particularly with respect to the properties of the hydrophobic thermoplastic polymer particles in combination with the hydrophilic polymer binders used therein.

More particularly it is an object of the present invention to provide required solvent resistance on the exposed image areas, while unexposed areas may still give a fast clean-up during the on-press processing.

Further advantages and embodiments of the present invention will become apparent from the following description.

SUMMARY OF THE INVENTION

The above mentioned objects are realized by providing a heat sensitive imaging element comprising, on a lithographic base with a hydrophilic surface thereupon, an image-forming layer including hydrophobic thermoplastic polymer particles and a hydrophilic (water-soluble, water-dispersable, alkali-dispersable or alkali-soluble) polymer binder, and, optionally, an infrared absorbing compound, characterized in that said hydrophobic polymer particles are containing structural chemical groups selected from the group consisting of amide, urethane, methacrylonitrile, crotononitrile, vinylidene cyanide, isocytosine, pyrrolidone, piperazine, cyanomethyl, cyanoethyl, cyanopropyl, cyanoaryl,

cyanoacrylate, primary amines, mono- or di- n-alkyl substituted amines, urea, imide, imine, triazine, sulfonamide, onium, melamine, pyrimidine, ureido-pyrimidone, pyridine, barbiturate, isocyanurate or imidazole.

A method for making a lithographic printing plate as a heat sensitive imaging element has also been described, said method comprising the steps of image-wise exposing to infrared light an imaging element according to the present invention and developing the said image-wise exposed imaging element by mounting it on a print cylinder of a printing press and applying an aqueous dampening liquid and/or ink to said imaging element while rotating said print cylinder. Moreover a method has been described wherein said imaging element is present on the press before starting image-wise exposure.

Use of hydrophobic polymer particles containing more than 0.1 % of nitrogen in a coating of a printing plate, and, more particularly use of said hydrophobic polymer particles in an image-forming layer of a heat sensitive imaging element as claimed, has also been claimed (for improving solvent resistance and/or run length).

Moreover use of hydrophobic polymer particles containing structural chemical groups selected from the group consisting of amide, urethane, acrylonitrile, vinylcarbazole, methacrylonitrile, crotononitrile, vinylidene cyanide, isocytosine, pyrrolidone, piperazine, cyanomethyl, cyanoethyl, cyanopropyl, cyanoaryl, cyanoacrylate, primary amines, mono- or di- n-alkyl substituted amines, urea, imide, imine, triazine, sulfonamide, onium, melamine, pyrimidine, ureido-pyrimidone, pyridine, barbiturate, isocyanurate or imidazole in a coating of a printing plate (for improving solvent resistance and/or run length) has also been claimed.

Specific features for preferred embodiments of the invention are set out in the dependent claims.

DETAILED DESCRIPTION OF THE INVENTION

With respect to the objects to be attained hydrophobic thermoplastic polymer particles prepared by making use of monomer units or building blocks containing nitrogen, and, more particularly those containing cyano-groups, copolymers of methacrylonitrile give the best results. So a heat sensitive imaging element comprising, on a lithographic base with a hydrophilic surface, an image-forming layer including such hydrophobic thermoplastic polymer particles, will be disclosed below as well as a method for making a lithographic printing plate comprising the steps of image wise exposing to infrared irradiation an imaging element according to the present invention; developing the obtained image-wise exposed imaging element by mounting it on a print cylinder of a printing press and apply an aqueous dampening liquid and/or ink to said imaged imaging element while rotating said print cylinder.

Regarding the objects of the present invention solvent resistance or chemical resistance towards cleaners for offset printing chemicals is obtained by introducing nitrogen atoms in the polymer particles, preferably by means of nitrile groups, amide bonds, urethane bonds, amino groups, in a sufficient amount as described. The solubility of the layer is consequently influenced by the presence of dipole-dipole interactions, hydrogen-bonding interactions or ionic interactions. The presence of a dipole moment in copolymers of cyano-containing monomer units in particular gives a large contribution to an increased solvent resistance. Besides dipole-dipole interactions hydrogen-bonding interactions or ionic interactions, presence of crystallinity in the employed hydrophobic polymer particles may attibute to the obtained chemical resistance, this in particlular for semi-crystalline polyamides, polyurethanes, etc.. Also onium containing structural components give an improved solvent resistance. However, one should take care that interactions between the hydrophilic polymer binder and the hydrophobic thermoplastic particles containing nitrogen, may influence plate performance, as e.g. with polymers containing polyacrylic acid, used as hydrophilic binder, wherein interaction with the thermoplastic particles should be avoided.

When cationic hydrophilic binders or other cationic components are used the water-based dispersions of the polymer particles are preferably stabilized: the colloidal stability of these particles is preferably obtained by making use of non-ionic or cationic surfactants or steric stabilizers (e.g. polyvinyl alcohol). When too much interaction between the hydrophilic binder and the hydrophobic thermoplastic particles is present, staining may occur on the non-imaged areas. In case of on-press processing of the hydrophobic particles and hydrophilic binder, the processing may be inhibited or retarded, due to said interactions. Of course interactions with the lithographic base (e.g. an anodized aluminum plate) may play an additional role in the on-press processing.

In one embodiment or the invention monomer units or building blocks are used which provide multiple-hydrogen bonds. An example of such interactions is the interaction between diacylated 2,6-diamino-pyridines and imide-containing molecules. In addition to the 4-substituted diacylated 2,6-diaminopyridines, 6-substituted diamino-triazines can be used as well. Another example is the complementary binding of thymine derivatives to di-amino triazine and recognition of uracil derivatives by di-amino triazine units. In particular cyano containing polymers give an improved solvent resistance, as, e.g., polymers containing cyano n-alkyl groups. Examples thereof are cyanomethyl (CN-CHR), cyanoethyl ($CN-CH_2-CH_2-R$) or cyanopropyl ($CN-CH_2-CH_2-CH_2-R$). Such cyano-group may be incorporated by polymer modification or by copolymerization of a cyano-containing monomer.

Use of such nitrogen-containing monomers which can give multiple hydrogen bonding has e.g. been described in the following references:

1) Lange,Ronald F.M.; Meijer, E.W.; Macromol.Symp.(1996),102,301-8,
2) Lange,Ronald F.M.; Meijer, E.W.; Belg.Pat.Appl. BE 1007778(1995),
3) Lange,Ronald F.M.; Meijer, E.W.; DSM Research, Geleen, The Neth., Macromolecules (1995), 28(3), 782-3.

A stronger multiple hydrogen-bonding complex can be used based on the ureido pyrimidone unit as described by E.W. Meijer et al:

1) Sijbesma,R.P.; Beijer,F.H.; Brunsveld,L.; Meijer,E.W. PCT Int. Appl. WO 98/14504 A1(1998);

2) Ky Hirschberg,J.H.K.; Beijer,F.H.; van Aert,Huub A.; Magusin, Pieter C. M. M.; Sijbesma, R.P.; Meijer, E.W. Macromolecules (1999), 32(8), 2696-2705;

3) Sijbesma,R.P.; Beijer,F.H.; Brunsveld,L.; Folmer, Brigitte J.B.; Ky Hirschberg, J.H.K.; Lange, R.F.M.; Lowe, J.K.L.; Meijer,E.W. Science (1997), 278(5343), 1601-1604.

The ureido pyrimidone unit can easily be prepared by reacting a isocytosine with an isocyanate. If a monomer is used with an isocyanate, such as TMI or isocyanatoethylmethacrylate, then a monomer is obtained which could be polymerized by addition polymerization. Such monomers can be used then in an emulsion copolymerisation in order to prepare water-based dispersions of polymer particles containing such ureido pyrimidone units. One can also prepare such hydrogen bonding molecules by endgroup modification, followed by dispersion of the water-insoluble polymer in water. In order to prepare such polymers synthetic procedures as described by Folmer et al. can be used (see Folmer, Brigitte J. B.; Sijbesma, Rint P.; Versteegen, Ron M.; van der Rijt, Joost A. J.; Meijer, E. W. Adv. Mater. (2000), 12(12), 874-878).

The thermoplastic polymer particles containing nitrogen in an amount of more than 0.1% by weight as disclosed in the present invention can be prepared by addition polymerization (e.g. free-radical emulsion copolymerization) or by condensation polymerization (e.g. polyurethanes, polyamides, polyamines, polyimides, polyimines, polyureas, etc.). The hydrophobic polymer particles used in the imaging element according to the present invention are prepared by means of monomers, or building blocks, consisting of the group of compounds having following structural formulae:

Acrylonitrile: CAS No. 107-13-1

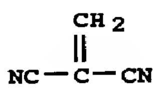
$$H_2C{=}CH{-}C{\equiv}N$$

Methacrylonitrile: CAS No. 4786-20-3

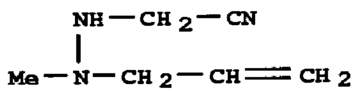
$$H_3C{-}CH{=}CH{-}C{\equiv}N$$

Crotononitrile, CAS No. 4786-20-3

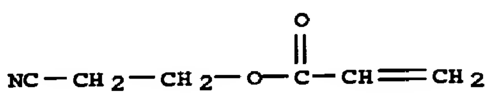
Vinylidene cyanide, CAS No. 922-64-5



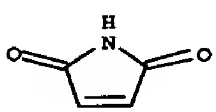
(2-Allyl-2-methylhydrazino)- Acetonitrile, CAS No. 16142-44-2



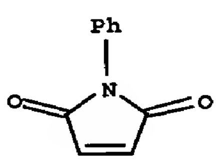
2-Cyanoethyl acrylate, CAS No. 106-71-8



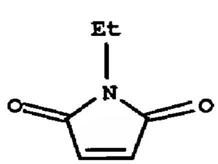
Maleimide, CAS No. 541-59-3



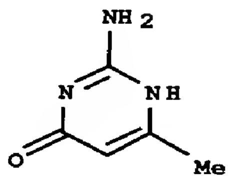
N-Phenylmaleimide, CAS No. 941-69-5



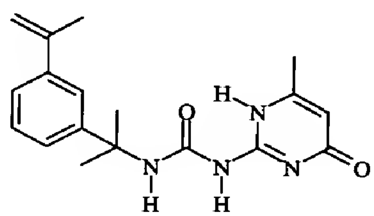
N-Ethylmaleimide, CAS No. 128-53-0



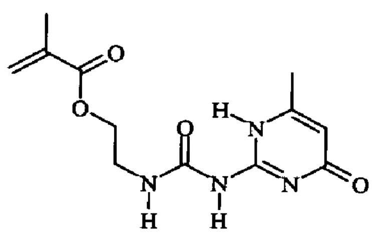
6-Methylisocytosine, CAS No. 3977-29-5



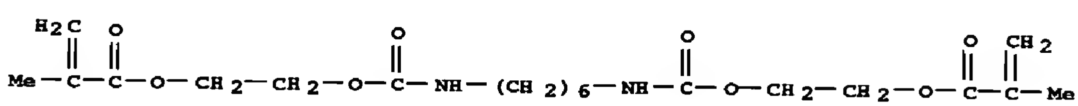
1-[1-(3-isopropenyl-phenyl)-1-methyl-ethyl]-3-(6-methyl-4-oxo-1,4-dihydro-pyrimidine-2-yl) urea



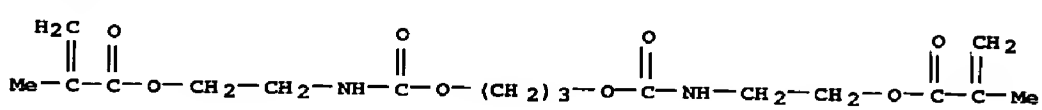
2-methyl-acrylic acid 2-[3-(6-methyl-4-oxo-1,4-dihydro-pyrimidin-2-yl) ureido] ethyl ester



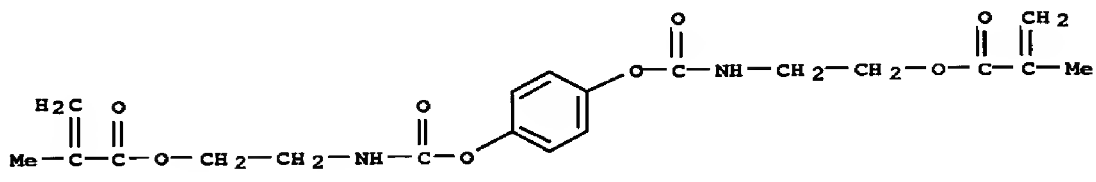
Hexamethylene-α,ω-bis(methacryloyloxyethyl)urethane, CAS No. 34100-36-2



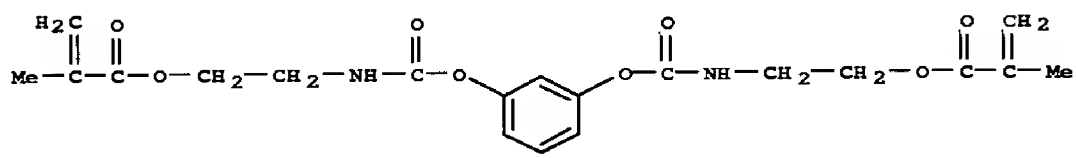
2-Propenoic acid, 2-methyl-, 4,10-dioxo-5,9-dioxa-3,11-diazatridecane-1,13-diyl ester, CAS No. 51265-06-6



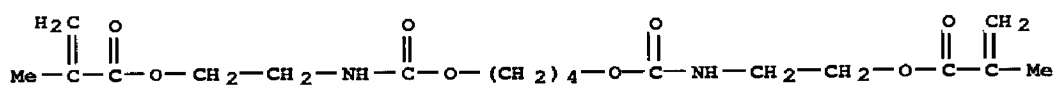
2-Propenoic acid, 2-methyl-, 1,4-phenylenebis(oxycarbonylimino-2,1-ethanediyl) ester, CAS No. 51265-08-8



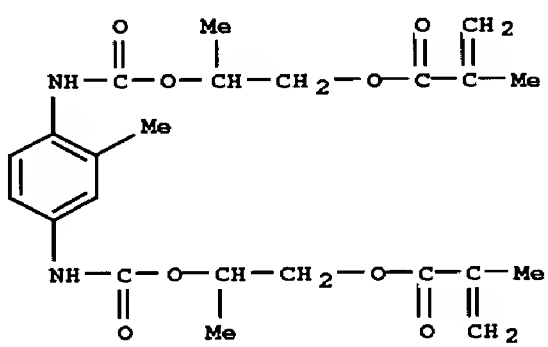
2-Propenoic acid, 2-methyl-, 1,3-phenylenebis(oxycarbonylimino-2,1-ethanediyl) ester, CAS No. 51265-09-9



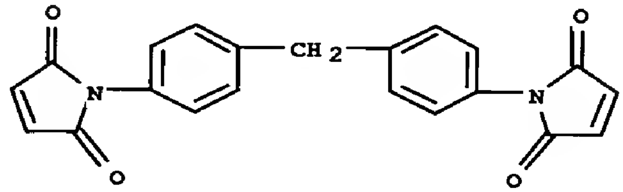
2-Propenoic acid, 2-methyl-, 4,11-dioxo-5,10-dioxa-3,12-diazatetradecane-1,14-diyl ester, CAS No. 51370-12-8



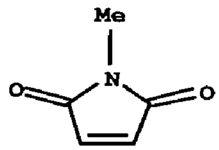
2-Propenoic acid, 2-methyl-, (2-methyl-1,4-phenylene)bis[iminocarbonyloxy(2-methyl-2,1-ethanediyl)] ester , CAS No. 127323-73-3



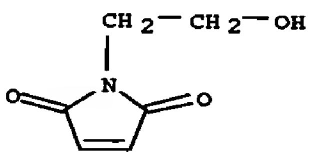
N,N'-(4,4'-Diphenylmethane)bismaleimide, CAS No. 13676-54-5



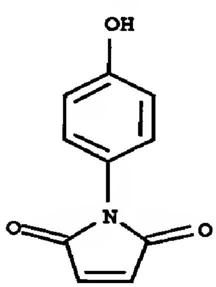
N-Methylmaleimide, CAS No. 930-88-1



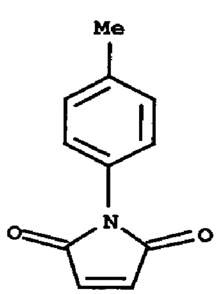
N-(2-Hydroxyethyl)maleimide, CAS No. 1585-90-6



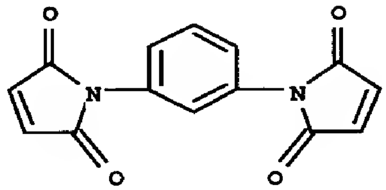
N-(p-Hydroxyphenyl)maleimide, CAS No. 7300-91-6



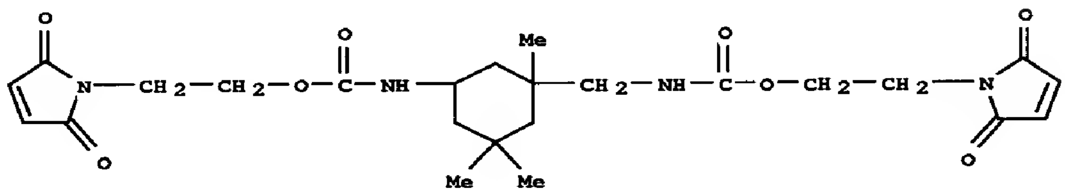
N-4-Tolylmaleimide, CAS No. 1631-28-3



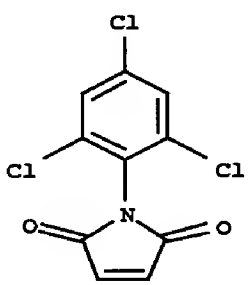
m-Phenylenebismaleimide, CAS No. 3006-93-7



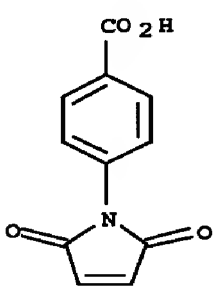
Carbamic acid, [5-[[[[2-(2,5-dihydro-2,5-dioxo-1H-pyrrol-1-yl)ethoxy]carbonyl]amino]methyl]-3,3,5-trimethylcyclohexyl]-, 2-(2,5-dihydro-2,5-dioxo-1H-pyrrol-1-yl)ethyl ester, CAS No. 203193-13-9



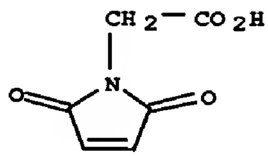
N-(2,4,6-Trichlorophenyl)maleimide, CAS No. 13167-25-4



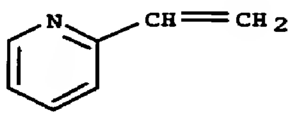
p-Maleimidobenzoic acid, CAS No. 17057-04-4



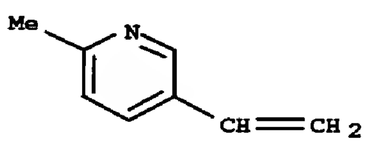
N-Maleimidoglycine, CAS No. 25021-08-3



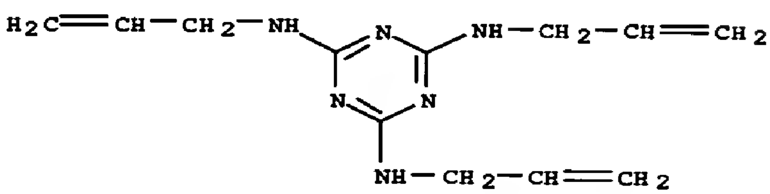
2-Vinylpyridine, CAS No. 100-69-6



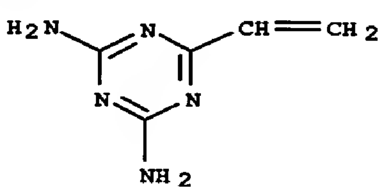
5-Vinyl-2-picoline, CAS No. 140-76-1



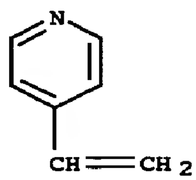
N,N',N''-Triallylmelamine, CAS No. 30360-21-5



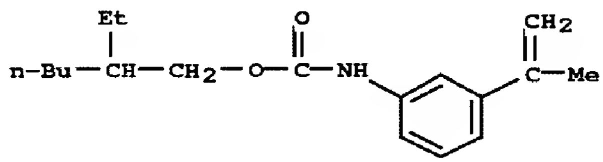
4,6-Diamino-2-vinyl-s-triazine, CAS No. 3194-70-5



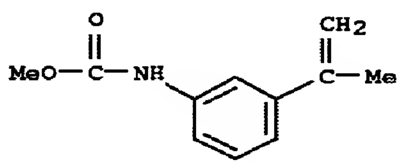
4-Vinylpyridine, CAS No. 100-43-6



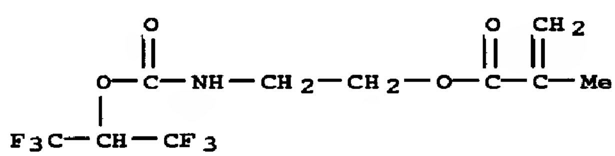
Carbamic acid, [3-(1-methylethenyl)phenyl]-, 2-ethylhexyl ester, CAS No. 152419-01-7



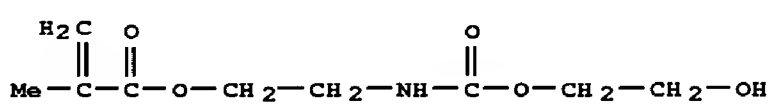
Carbamic acid, [3-(1-methylethenyl)phenyl]-, methyl ester, CAS No. 152418-98-9



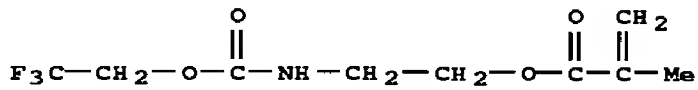
2-Propenoic acid, 2-methyl-, 2-[[[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]carbonyl] amino]ethyl ester, CAS No. 137130-28-0



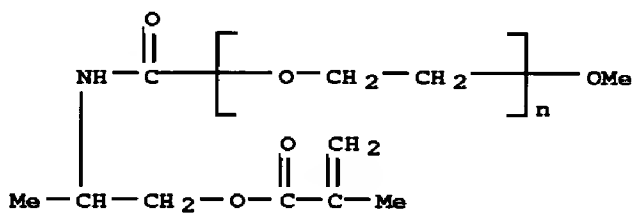
2-Propenoic acid, 2-methyl-, 2-[[(2-hydroxyethoxy)-carbonyl]amino]ethyl ester , CAS No. 151362-30-0



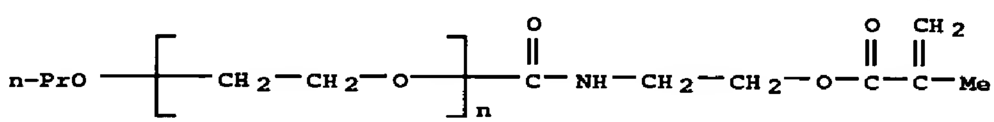
2-Propenoic acid, 2-methyl-, 2-[[(2,2,2-trifluoroethoxy)carbonyl]-amino]ethyl ester, CAS No. 103527-92-0



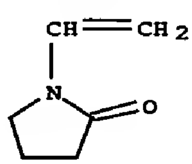
α-[[[1-methyl-2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]amino]-carbonyl]-□-methoxy- Poly(oxy-1,2-ethanediyl), CAS No. 178490-91-0



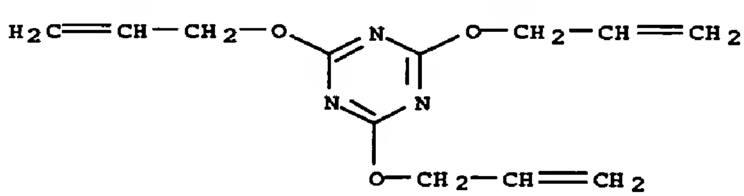
α-[[[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]amino]-carbonyl]-ω-propoxy- Poly(oxy-1,2-ethanediyl), CAS No. 280569-16-6



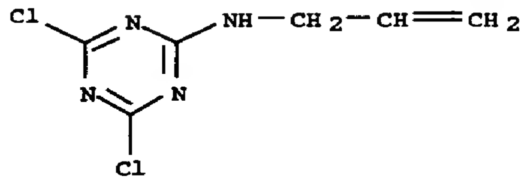
N-Vinyl-2-pyrrolidone, CAS No. 88-12-0



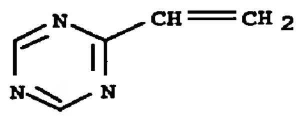
2,4,6-Tris(allyloxy)-s-triazine, CAS No. 101-37-1



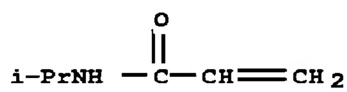
2-Allylamino-4,6-dichloro-s-triazine, CAS No. 30369-80-3



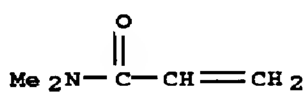
1,3,5-Triazine, 2-ethenyl- , CAS No. 45589-18-2



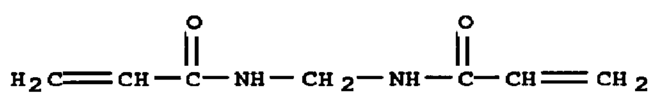
N-Isopropylpropenamide, CAS No. 2210-25-5



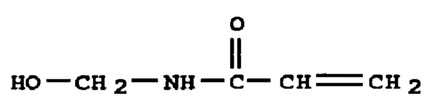
N,N-Dimethylpropenamide, CAS No. 2680-03-7



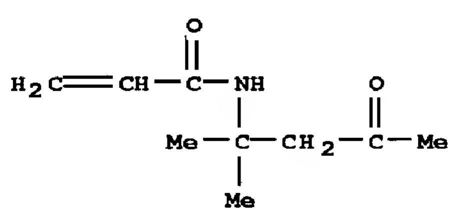
N,N'-Methylenediacrylamide, CAS No. 110-26-9



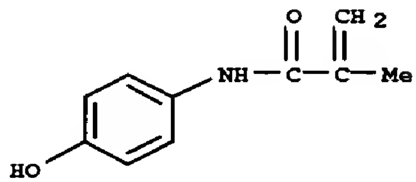
N-Methylolacrylamide, CAS No. 924-42-5



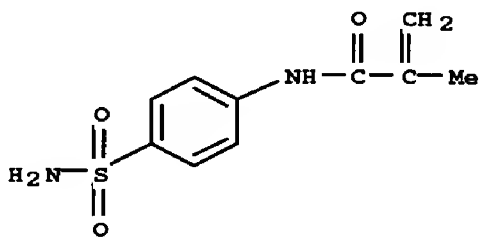
Diacetone acrylamide, CAS No. 2873-97-4



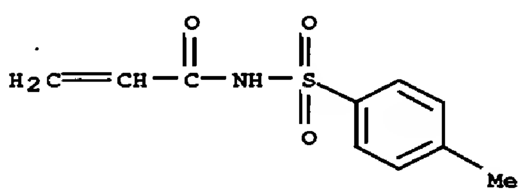
p-Methacrylamidophenol, CAS No. 19243-95-9



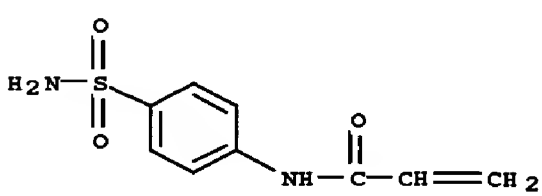
4-Methacrylamidobenzenesulfonamide, Cas No. 56992-87-1



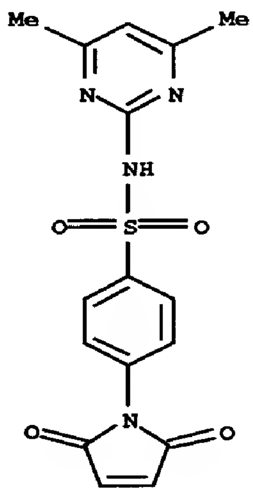
N-[(4-methylphenyl)sulfonyl]- 2-Propenamide, CAS No. 131290-90-9



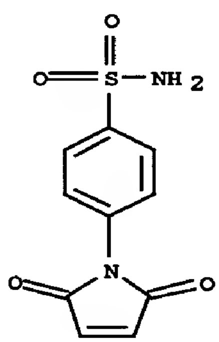
N-(p-Aminosulfonylphenyl)acrylamide, CAS No. 2621-99-0



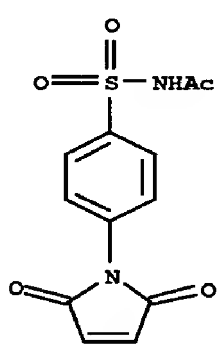
4-(2,5-dihydro-2,5-dioxo-1H-pyrrol-1-yl)-N-(4,6-dimethyl-2-pyrimidinyl)- Benzenesulfonamide, CAS No. 233761-16-5



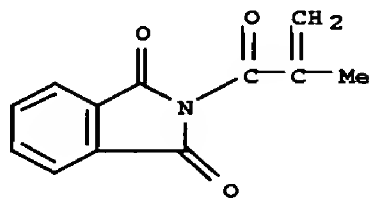
4-(2,5-dihydro-2,5-dioxo-1H-pyrrol-1-yl)- Benzenesulfonamide, CAS No. 7300-97-2



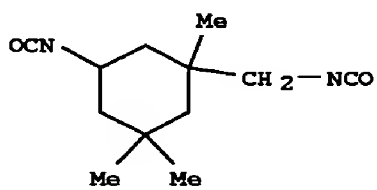
N-(N-Acetyl-p-sulfamoylphenyl)maleimide, CAS No. 1886-78-8



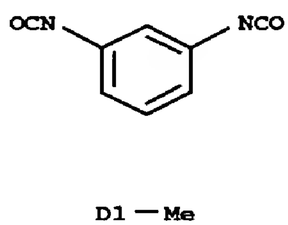
N-Methacryloylphthalimide, CAS No. 40459-78-7



Isophorone diisocyanate, CAS No. 4098-71-9



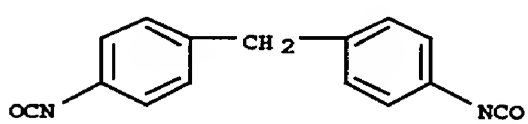
Tolylene isocyanate, CAS No. 26471-62-5



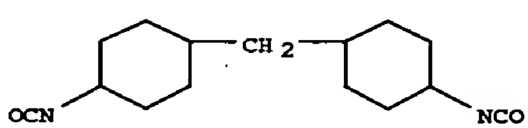
Hexane 1,6-diisocyanate, CAS No. 822-06-0

$OCN-(CH_2)_6-NCO$

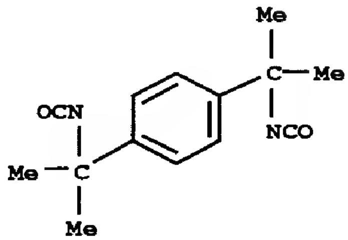
p,p'-Methylenebis(phenyl isocyanate), Cas No. 101-68-8



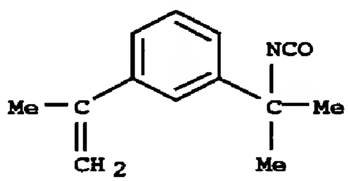
Methylenedi-4-cyclohexylene diisocyanate, Cas No. 5124-30-1



p-Tetramethylxylylene diisocyanate, CAS No. 2778-41-8



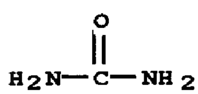
m-Isopropenylcumyl isocyanate, CAS No. 2094-99-7



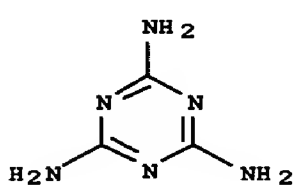
N-(2-Aminoethyl)ethylenediamine, CAS No. 111-40-0

$$H_2N—CH_2—CH_2—NH—CH_2—CH_2—NH_2$$

Urea, CAS No. 57-13-6



Melamine, CAS No. 108-78-1



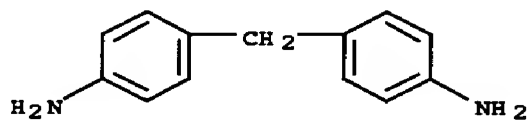
Hexamethylenediamine, CAS No. 124-09-4

$$H_2N—(CH_2)_6—NH_2$$

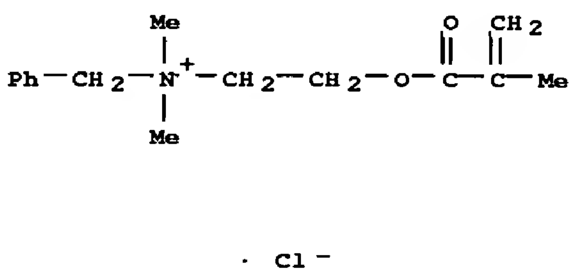
N,N-Diethanolamine, CAS No. 111-42-2

$$HO-CH_2-CH_2-NH-CH_2-CH_2-OH$$

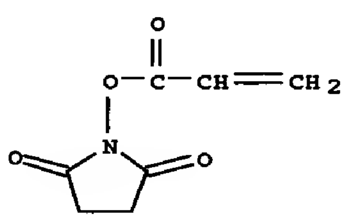
Methylenedianiline, CAS No. 101-77-9



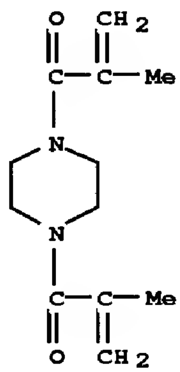
Benzyl(methacryloyloxyethyl)dimethylammonium chloride, CAS No. 46917-07-1



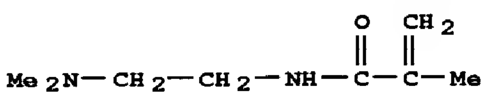
N-Succinimidyl acrylate, CAS No. 38862-24-7



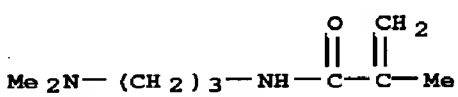
1,4-Dimethacryloylpiperazine, CAS No. 17308-56-4



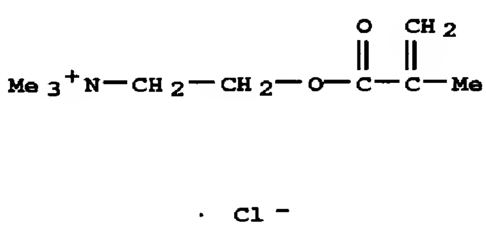
N-[2-(Dimethylamino)ethyl]methacrylamide, CAS No. 13081-44-2



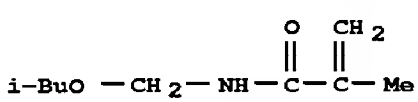
N-[3-(N,N-Dimethylamino)propyl]methacrylamide, CAS No. 5205-93-6



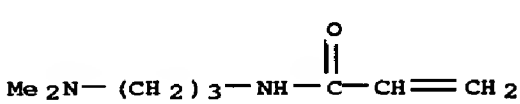
[2-(Methacryloyloxy)ethyl]trimethylammonium chloride, CAS No. 5039-78-1



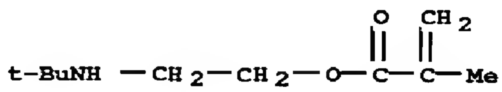
N-iso-Butoxymethylmethacrylamide, CAS No. 4548-27-0



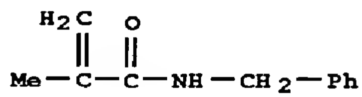
N-[3-(Dimethylamino)propyl]acrylamide, CAS No. 3845-76-9



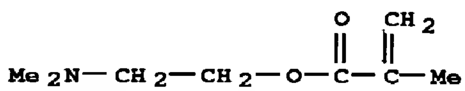
N-tert-Butylaminoethyl methacrylate, CAS No. 3775-90-4



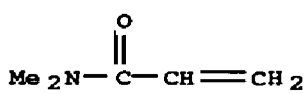
N-Benzylmethacrylamide, CAS No. 3219-55-4



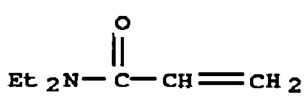
N,N-Dimethylethanolamine methacrylate, CAS No. 2867-47-2



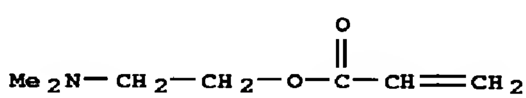
N,N-Dimethylacrylamide, CAS No. 2680-03-7



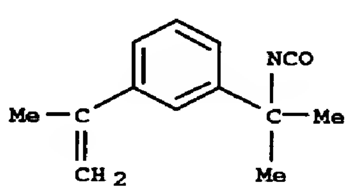
N,N-Diethylacrylamide, CAS No. 2675-94-7



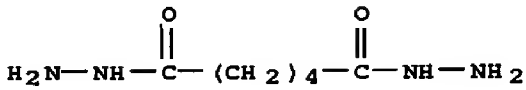
Dimethylaminoethyl acrylate, CAS No. 2439-35-2



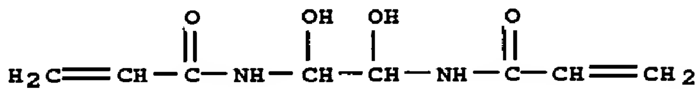
m-Isopropenylcumyl isocyanate, CAS No. 2094-99-7



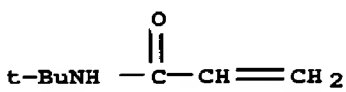
Adipic acid, dihydrazide, CAS No. 1071-93-8



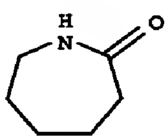
Dihydroxyethylenebis(acrylamide), CAS No. 868-63-3



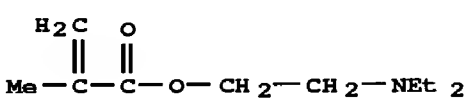
tert-Butylacrylamide, CAS NO. 107-58-4



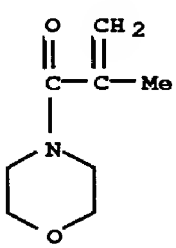
Caprolactam, CAS No. 105-60-2



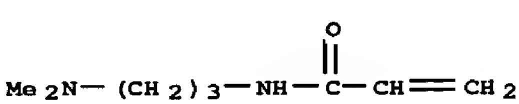
N,N-Diethylaminoethyl methacrylate, CAS No. 105-16-8



N-Methacryloylmorpholine, CAS No. 5117-13-5



N-[3-(Dimethylamino)propyl]acrylamide, CAS No. 3845-76-9



Ethylenimine, CAS No. 151-56-4

Trimethylenediamine, CAS No. 109-76-2

$H_2N—CH_2—CH_2—CH_2—NH_2$

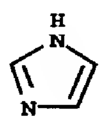
1,2-Ethanediamine , CAS No. 107-15-3

$H_2N—CH_2—CH_2—NH_2$

1,4-Butanediamine , CAS No. 110-60-1

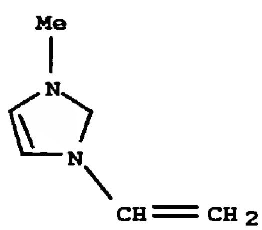
$H_2N—(CH_2)_4—NH_2$

Vinylimidazole, CAS No. 29383-23-1

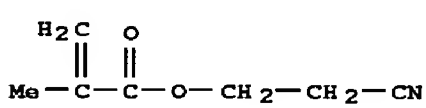


$D1—CH{=}CH_2$

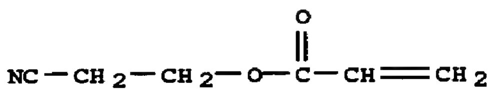
1-ethenyl-3-methyl-1H-Imidazolium, Cas No. 45534-45-0



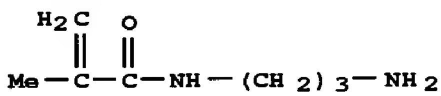
Cyanoethyl methacrylate, CAS No. 4513-53-5



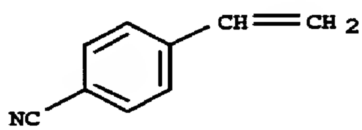
2-Cyanoethyl acrylate, CAS No. 106-71-8



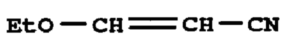
N-(3-Aminopropyl)methacrylamide, CAS No. 86742-39-4



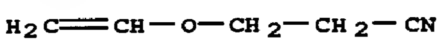
p-Cyanostyrene, CAS No. 3435-51-6



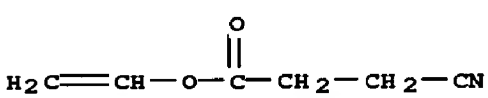
3-Ethoxyacrylonitrile, CAS No. 61310-53-0



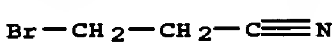
2-Cyanoethyl vinyl ether, CAS No. 15678-32-7



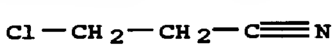
Propanoic acid, 3-cyano-, ethenyl ester, CAS No. 160745-18-6



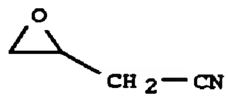
3-Bromopropionitrile, CAS No. 2417-90-5



3-Chloropropionitrile, CAS No. 542-76-7



3,4-Epoxybutyronitrile, CAS No. 624-58-8



3-Aminopropionitrile, CAS No. 151-18-8

$H_2N-CH_2-CH_2-C\equiv N$

3-Hydroxypropionitrile, CAS No. 109-78-4

$HO-CH_2-CH_2-C\equiv N$

4-Cyanobutyric acid, CAS No. 39201-33-7

$NC-(CH_2)_3-CO_2H$

As can be derived from the structures given above, the nitrogen atom may be introduced via the monomer or another building block in the preparation of the hydrophobic thermoplastic polymer particles.

The nitrogen atoms may also be introduced via surfactants containing nitrogen atoms, used in order to stabilize aqueous dispersions or via absorption on the surface of the thermoplastic polymer particle of polymers containing nitrogen atoms. The thermoplastic polymer particles as described are, in a preferred embodiment of the present invention, applied as water based dispersions. The water-based dispersions of the hydrophobic thermoplastic polymer particles of the present invention can be prepared by polymerization in a water-based system, e.g. by emulsion polymerization, or by means of dispersing techniques of the water-insoluble polymers into water.

The said polymer particles can be dispersed in water by several techniques, well-known in the art, as e.g. by dispersing a solid polymer particle, making use therefor of surfactants or other stabilizing agents, or by evaporating a water-based polymer emulsion, containing a water-immiscible organic solvent (as e.g ethyl acetate).

According to the present invention a heat sensitive imaging element is thus provided, wherein said element comprises, on a lithographic base with a hydrophilic surface, an image-forming layer including hydrophobic thermoplastic polymer particles, a hydrophilic polymer binder and a compound absorbing infrared radiation, coated in said image forming layer or in a layer adjacent thereto, characterized in that said hydrophobic polymer particles are containing chemical groups or units in their structure, said groups or units being selected from the group consisting of amide, urethane, methacrylonitrile, cyanoethyl, cyanoacrylate, primary amines, mono- or di- n-alkyl substituted amines, urea, imide, imine, triazine, sulfonamide, onium, melamine, pyrimidine, ureido-pyrimidone, pyridine, barbiturate, isocyanurate and imidazole.

In a preferred embodiment of the present invention the heat-sensitive imaging element contains a hydrophilic polymer binders which are water-soluble, water-dispersable, alkali-dispersable or alkali-soluble.

In another embodiment said heat sensitive imaging element according to the present invention has hydrophobic thermoplastic polymer particles consisting of a homopolymer or copolymer of monomers selected from the group consisting of styrene, tert.-butylstyrene, methylmethacrylate, para-methylstyrene, methacrylonitrile, N-alkyl substituted acrylamides, N-alkyl substituted methacrylamides and maleimides.

In a further preferred embodiment in the heat sensitive imaging element according to the present invention the hydrophobic thermoplastic polymer particles are containing nitrile groups and, even more preferably, the heat sensitive imaging element according to the present invention has hydrophobic thermoplastic polymer particles consisting of a homopolymer or copolymer of methacrylonitrile.

In another embodiment the heat sensitive imaging element according to the present invention has hydrophobic thermoplastic polymer particles consisting of a homopolymer or copolymer selected from the group of polymer types consisting of polyurethanes, polyamides, polyamines, polyureas and polyimides.

The imaging element of the present invention further preferably has hydrophobic thermoplastic particles having nitrogen-containing units which form multiple hydrogen bonds, and more preferably, the said thermoplastic particles have ureido pyrimidone units.

In a preferred embodiment of the present invention the imaging material has hydrophobic polymer particles having an average particle size diameter of less than 0.5 µm, and even more preferably an average particle size diameter in the range from 0.015 to 0.150 µm.

According to the present invention the imaging element has hydrophobic thermoplastic polymer particles which are present in the image forming layer in an amount of at least 50 wt%.

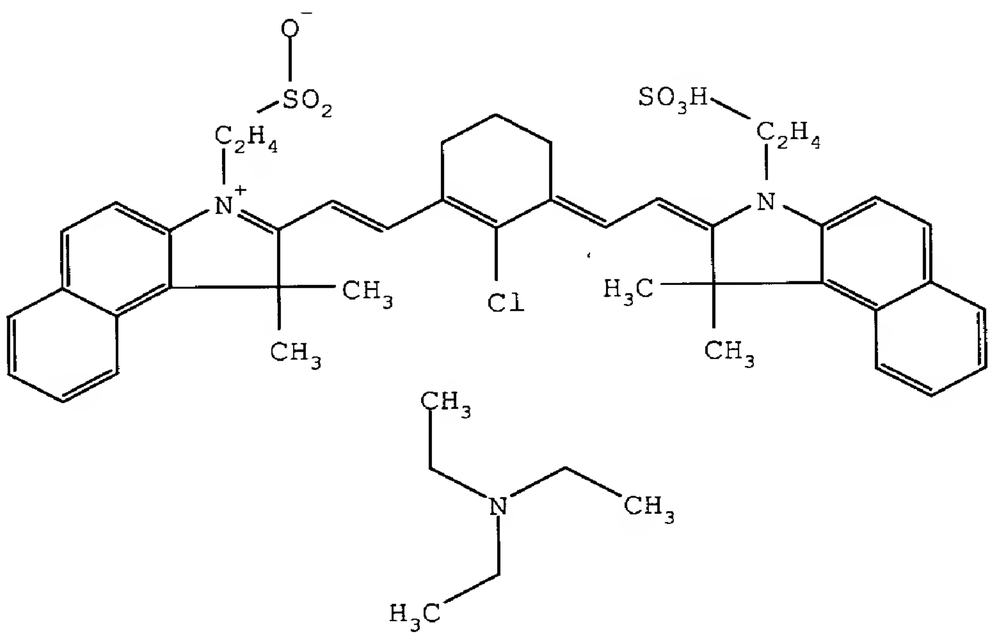
In another preferred embodiment the imaging element according to the present invention has a hydrophilic binder polymer which is present in said image forming layer and/or a layer adjacent thereto.

In the imaging element according to the present invention the said hydrophilic polymer binder present in said image forming layer and/or a layer adjacent thereto more preferably contains carboxylic acid groups.

In another embodiment the said hydrophilic polymer binder which is present in said image forming layer and/or a layer adjacent thereto of the imaging element according to the present invention, contains acrylic acid, methacrylic acid, itaconic acid, crotonic acid or maleïc acid moieties.

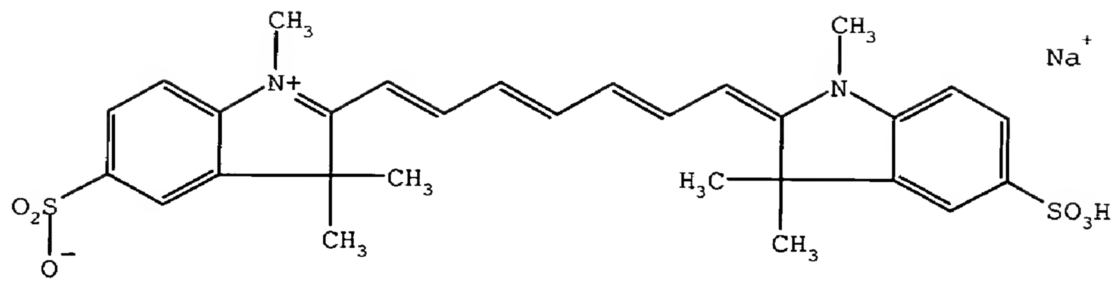
According to the present invention the imaging element has an infrared absorbing compound being an anionic infrared cyanine dye absorbing infrared radiation in the wavelength range from 800 to

1100nm. In a preferred embodiment of the present invention, in the imaging element the infrared absorbing compound is present in said image forming layer or in a layer adjacent thereto. The image forming layer and/or a layer adjacent thereto thus comprises, in accordance with the present invention, an anionic infrared(IR) cyanine dye, which serves as a light to heat converting compound. A mixture of anionic infrared-cyanine dyes may be used, but it is preferred to use only one anionic IR-cyanine dye. Particularly useful anionic IR-cyanine dyes are IR-cyanines dyes with at least two sulphonic groups. Still more preferably are IR-cyanines dyes with two indolenine and at least two sulphonic acid groups. Most preferable is compound I having a chemical structure as given hereinafter.



(I)

Also the compound II having a structure as indicated furtheron, gives good results.



(II)

The amount of anionic IR-cyanine dye contained in the image-forming layer is preferably between 1% by weight and 40% by weight, more preferably between 2% by weight and 30% by weight and even most preferably between 5% by weight and 20% by weight of said image-forming layer.

In a preferred embodiment according to the present invention the imaging element has a surface, wherein said surface is a lithographic surface, present on a metal support, being a plate or a print cylinder, and wherein, in a further preferred embodiment said metal support is anodized aluminum.

According to the present invention a method for making a lithographic printing plate is further offered, said method comprising the steps of

1) image-wise exposing to infrared light an imaging element according to the present invention as disclosed hereinbefore;

2) developing the image-wise exposed imaging element by mounting it on a print cylinder of a printing press and applying an aqueous dampening liquid and/or ink to said imaging element while rotating said print cylinder.

According to the present invention a method is also offered for making a lithographic printing plate as disclosed hereinbefore, wherein said imaging element is present on the press before starting image-wise exposure to infrared light.

To summarize: use of hydrophobic thermoplastic polymer particles as claimed, in combination with a hydrophilic polymer binder in a plate, based on image-wise fusing of polymer particles has never been described until now.

The objects of the present invention are moreover fully obtained as will be illustrated hereinafter in the examples, after image-wise exposure to infrared radiation of a plate according to the present invention and subsequent development by mounting it on a print cylinder of a printing press and application of an aqueous dampening liquid and/or ink to said image imaging element while rotating said print cylinder. Making use of image-wise fusing of hydrophobic thermoplastic polymer particles containing nitrogen in an amount as claimed in the present invention, clearly gives an improved solvent resistance on the infrared-exposed areas, while the non-exposed areas are developed on-press and the lithographic aluminum base with very good hydrophilicity is set free. Use of a hydrophilic polymer binder, such as polyacrylic acid, polyvinyl alcohol or acrylic acid copolymers, gives a fast clean-up during the on-press processing, even though the polymer particles have a very low solubility.

As has been disclosed in EP-A 0 849 091 polyacrylonitrile and polyvinylcarbazole are very useful polymers providing hydrophobic thermoplastic polymer particles having an average particle size of from 40 nm to 150 nm in order to guarantee excellent printing properties and convenient ecological development of lithographic printing plates and to provide a heat sensitive imaging element for making lithographic printing plates with an improved sensitivity, a high throughput and less scumming. At the time when that application was filed, the effect on solvent resistance as intensively studied now, was not known and only within the context of the present invention it has been confirmed that also acrylonitrile and vinylcarbazole monomers give rise to hydrophobic polymers with an improved solvent resistance and/or run length for imaging elements as claimed.

According to the present invention use of hydrophobic polymer particles containing more than 0.1 % of nitrogen in a coating of a printing plate for improving solvent resistance and/or run length

has also been claimed and more particularly use of hydrophobic polymer particles containing more than 0.1 % of nitrogen in an image-forming layer of a heat sensitive imaging element according to the present invention as disclosed before, for improving solvent resistance and/or run length.

According to the present invention use of hydrophobic polymer particles containing structural chemical groups selected from the group consisting of amide, urethane, acrylonitrile, vinylcarbazole, methacrylonitrile, crotononitrile, vinylidene cyanide, isocytosine, pyrrolidone, piperazine, cyanomethyl, cyanoethyl, cyanopropyl, cyanoaryl, cyanoacrylate, primary amines, mono- or di- n-alkyl substituted amines, urea, imide, imine, triazine, sulfonamide, onium, melamine, pyrimidine, ureido-pyrimidone, pyridine, barbiturate, isocyanurate or imidazole in a coating of a printing plate for improving solvent resistance and/or run length is envisaged.

While the present invention will, in the examples hereinafter, be described in connection with preferred embodiments thereof, it will be understood that it is not intended to limit the invention to those embodiments.

Examples

EXAMPLE 1

<u>Preparation of the lithographic base</u>

A 0.30 mm thick aluminum foil was degreased by immersing the foil in an aqueous solution containing 5 g/l of sodium hydroxide at 50°C and rinsed with demineralized water. The foil was then electrochemically grained using an alternating current in an aqueous solution containing 4 g/l of hydrochloric acid, 4 g/l of hydroboric acid and 5 g/l of aluminum ions at a temperature of 35°C and a current density of 1200 A/m^2 in order to form a surface topography with an average center-line roughness Ra of 0.5 mm.

After rinsing with demineralized water the aluminum foil was then etched with an aqueous solution containing 300 g/l of sulfuric acid at 60°C for 180 seconds and rinsed with demineralized water at 25°C for 30 seconds.

The foil was subsequently subjected to anodic oxidation in an aqueous solution containing 200 g/l of sulfuric acid at a temperature of 45°C, a voltage of about 10 V and a current density of 150 A/m^2 for about 300 seconds to form an anodic oxidation film of 3.00 g/m^2 of Al_2O_3, then washed with demineralized water and post-treated with a solution containing polyvinyl phosphonic acid, rinsed with demineralized water at 20°C, during 120 seconds, follwed by drying.

Preparation of the imaging elements

An imaging element was produced by preparing the following (comparative) coating composition 1, which was coated onto the lithographic base described above, in an amount of 30 g/m^2 (wet coating amount), followed by drying at 35°C, resulting in a dry layer coating having a thickness of 0.8 µm.

Imaging elements 2-12 according to the invention were produced in a similar way, making use from the coating compositions 2-12, described below.

Preparation of the coating composition 1 (Comparative composition)

To 10.0 g of a 20 wt% dispersion of a poly(styrene) homopolymer having a particle size diameter of 75nm, which was stabilized with a surfactant (1.5 wt% vs. the polymer) in deionized water was added 26.7 g of a 1 wt% solution of compound I.

To the solution solution described above was added 36.1 g of deionized water and 26.7 g of a 1.5 wt% solution of Glascol E15 (polyacrylic acid, commercially available from Allied Colloids Ltd., UK). Furthermore 0.5 ml of a fluor substituted surfactant solution was added (5 wt% of a solution of tetra-ethylammonium n-perfluoro-octane sulfonate in water/ethanol 50/50).

Preparation of the coating composition 2 (inventive)

To 10.0 g of a 20 wt% dispersion of poly(styrene-co-acrylonitrile) (having a styrene/acrylonitrile weight ratio of 95 /5; with

a particle size diameter of 70nm) stabilized with a surfactant (1.5 wt% vs. polymer) in deionized water was added 26.7 g of a 1 wt% solution of compound I.

To the above obtained solution was added 36.1 g of deionized water and 26.7 g of a 1.5 wt% solution of Glascol E15 (polyacrylic acid commercially available from Allied Colloids Ltd.,UK). Furthermore 0.5 ml of a fluor substituted surfactant solution was added (5 wt% solution of tetraethylammonium n-perfluoro-octane sulfonate in water/ethanol 50/50).

Preparation of the coating composition 3 (inventive)

To 10.0 g of a 20 wt% dispersion of poly(styrene-co-acrylonitrile) (having a styrene/acrylonitrile weight ratio of 85 /15; and a particle size diameter of 60nm) stabilized with a surfactant (1.5 wt% vs. polymer) in deionized water, was added 26.7 g of a 1 wt% solution of compound I.

To the above obtained solution was added 36.1 g of deionized water and 26.7 g of a 1.5 wt% solution of Glascol E15 (polyacrylic acid commercially available from Allied Colloids Ltd., UK). Furthermore 0.5 ml of a fluor substituted surfactant solution was added (5 wt% solution of tetraethylammonium n-perfluoro-octane sulfonate in water/ethanol 50/50).

Preparation of the coating composition 4 (inventive)

To 10.0 g of a 20 wt% dispersion of poly(styrene-co-acrylonitrile) (having a styrene/acrylonitrile weight ratio of 66.3/33.7; and a particle size diameter of 60nm) stabilized with a surfactant (1.5 wt% vs. polymer) in deionized water was added 26.7 g of a 1 wt% solution of compound I.

To the above obtained solution was added 36.1 g of deionized water and 26.7 g of a 1.5 wt% solution of Glascol E15 (polyacrylic acid commercially available from Allied Colloids Ltd., UK). Furthermore 0.5 ml of a fluor substituted surfactant solution was added (5 wt% solution of tetraethylammonium n-perfluoro-octane sulfonate in water/ethanol 50/50).

Preparation of the coating composition 5 (inventive)

To 10.0 g of a 20 wt% dispersion of poly(styrene-co-acrylonitrile) (having a styrene/acrylonitrile weight ratio of 66.3 /33.7; and a particle size diameter of 50nm) stabilized with a surfactant (1.5% w/w vs. polymer) in deionized water was added 26.7 g of a 1 wt% solution of compound I.

To the above obtained solution was added 36.1 g of deionized water and 26.7 g of a 1.5 wt% solution of Glascol E15 (polyacrylic acid commercially available from Allied Colloids Ltd., UK). Furthermore 0.5 ml of a fluor substituted surfactant solution was added (5 wt% solution of tetraethylammonium n-perfluoro-octane sulfonate in water/ethanol 50/50).

Preparation of a printing plate and making copies of the original

Each of the imaging elements 1-5 as described above was subjected to a scanning diode laser, emitting laser radiation having a wavelength of 830 nm (scan speed: 1 m/s, at 2540 dpi and with a power on the plate surface of 44mW).

After imaging the plate was processed on a press (Heidelberg GTO46), using Van Son rubberbase VS2329 ink and Rotamatic fountain in order to remove the unexposed areas, resulting in a negative working lithographic printing plate.

Table 1 summarizes the results in terms of sensitivity (expressed in mJ/cm^2), runlength (the longer, the better) and chemical resistance (the more "+"-signs, the better the resistance).

Table 1

Coat. Composition	Sensitivity	Runlength	Chemical resistance
1 (comp.)	230	9000	Reference
2 (inv.)	225	9000	+
3 (inv.)	225	>15000	++
4 (inv.)	235	>15000	+++

5 (inv.)	225	>15000	+++

For about the same sensitivity, the runlength and chemical resistance was improved to a remarkable extent for the inventive coating compositions.

Chemical resistance against press chemicals was tested by means of a procedure wherein the printing plate which was processed on-press, was brought in contact, during 1 minute, with several chemicals and subsequently wipped off, making use of a wet cotton pad. Subsequently the lithographic plate performance was tested again. The results for the chemical resistance, obtained by this test, have been summarized in table 2. Increasing amounts of acrylonitrile in the polymer latex clearly provide a better chemical resistance. The image was checked in a full plane area and in a screen plane (grid).

Table 2

Coating comp.	Solvent A75	Meter X	RC910	RC95	G642b
1 (comp.)	Image totally removed	Image totally removed	Screen plane slightly Destroyed	Screen plane Destroyed	Screen plane slightly Destroyed
2 (inv.)	Image slightly destroyed	Almost no image damage	Almost no screen plane damage	Screen plane slightly destroyed	Almost no screen plane
3 (inv.)	OK	Almost no damage	OK	OK	OK
4 (inv.)	OK	OK	OK	OK	OK

5(inv.)	OK	OK	OK	OK	OK

EXAMPLE 2.

Similar coating compositions as in Example 1 were prepared and evaluated, said coatings containing 75 wt% of water-dispersed polymer particles,10 wt% of IR-dye compound and 15% of polyacrylic acid. The type of polymer particles was varied and compared to a polystyrene homopolymer emulsion and an emulsion polymer based on styrene/ acrylonitrile as used in example 1. Employed polymer types of the thermoplastic particle for compositions 6-12 have been given below.

*Comparative coating composition 6 contains *a polystyrene homopolymer latex* (particle size : 75 nm).

*Inventive coating composition 7 contains *a styrene/acrylonitrile copolymer* (monomer weight ratio styrene/acrylonitrile:64.4/34.7, particle size : 55 nm)

*Inventive coating composition 8 contains a *styrene/methacrylonitrile copolymer latex* (monomer weight ratio styrene/methacrylonitrile:60.8/39.2, particle size : 66 nm)

*Inventive coating composition 9 contains a *styrene/N-isopropylacrylamide copolymer latex* (monomer weight ratio styrene/ N-isopropylacrylamide:85/15, particle size : 67 nm).

*Inventive coating composition 10 contains a *styrene/N-isopropylacrylamide copolymer latex* (monomer weight ratio styrene/ N-isopropylacrylamide:70/30, particle size : 57 nm).

*Comparative coating composition 11 contains a latex based on a *styrene /4-(2,5-dihydro-2,5-dioxo-1H-pyrrol-1-yl)-N-(4,6-dimethyl-2-pyrimidinyl)- Benzenesulfonamide copolymer* (weight ratio 95/5, particle size : 65 nm)

*Comparative coating composition 12 contains a latex based on a *copolymer of styrene and N,N',N''-Triallylmelamine* (99/1 weight ratio, particle size : 69 nm).

The results obtained for the coating compositions 6-12, have been summarized in Table 3 hereinafter.

The chemical resistance of these printing plates was tested further by treating the plate during 1 minute with several chemicals and subsquently wiping off, using a wet cotton pad. These plates were subsequently tested again in a printing experiment in order to see whether or not the image was damaged.

In the table below an indication has been given of the level of damage due to the solvent treatment (significance of the figures: 1 = image totally removed, and/or full plane damaged; 2= full plane = slightly damaged; 3 = no damage = OK; 1.5 = screen plane damaged, full plane OK; 2.5 = screen plane slightly damaged, full plane = OK). The results have been summarized in Table 4 following Table 3 hereinafter.

Table 3

Coating comp.	Sensitivity mJ/cm^2	Runlength	Chemical resistance
6 (comp.)	235	7000	Reference
7 (inv.)	235	>15000	+++
8 (inv.)	230	15000	+++
9 (inv.)	310	10000	++
10 (inv.)	>350	10000	++
11 (comp.)	240	4000	+
12 (comp.)	205	4000	+

The listed chemicals, such as Solvent A75, Meter X, RC95, RC95, and CR642B are well-known typical agressive chemicals used in offset printing which could damage the plate.

Table 4

Coating comp.	Solvent A75	Meter X	RC95	RC910	CR642B
6	0	0	1.5	1.5	1.5
7	3	3	2.5	3	3
8	3	3	2.5	3	3
9	3	0	2.5	3	3
10	3	1	2.5	3	3
11	1.5	2.5	1.5	1.5	1.5
12	0	0	1.5	2.5	3

The results obtained are fully in accordance with the conclusions to be drawn from those in Table 3, namely, that the coating compositions according to the invention, indicated as "inventive coatings" are fully providing properties properties as requested in the objects of the present invention.

Having described in detail preferred embodiments of the current invention, it will now be apparent to those skilled in the art that numerous modifications can be made therein without departing from the scope of the invention as defined in the appending claims.

[CLAIMS]

1. A heat sensitive imaging element comprising, on a lithographic base with a hydrophilic surface thereupon, an image-forming layer including hydrophobic thermoplastic polymer particles and a hydrophilic polymer binder, and, optionally, an infrared absorbing compound, characterized in that said hydrophobic polymer particles are containing structural chemical groups selected from the group consisting of amide, urethane, methacrylonitrile, crotononitrile, vinylidene cyanide, isocytosine, pyrrolidone, piperazine, cyanomethyl, cyanoethyl, cyanopropyl, cyanoaryl, cyanoacrylate, primary amines, mono- or di- n-alkyl substituted amines, urea, imide, imine, triazine, sulfonamide, onium, melamine, pyrimidine, ureido-pyrimidone, pyridine, barbiturate, isocyanurate or imidazole.

2. A heat sensitive imaging element according to claim 1, wherein said hydrophilic polymer binder is a water-soluble, water-dispersable, alkali-dispersable or alkali-soluble polymer.

3. A heat sensitive imaging element according to claim 1 or 2, wherein the hydrophobic thermoplastic polymer particles consist of a homopolymer or copolymer of monomers selected from the group consisting of styrene, tert.-butylstyrene, methylmethacrylate, para-methylstyrene, methacrylonitrile, N-alkyl substituted acrylamides, N-alkyl substituted methacrylamides and maleimides.

4. An imaging material according to any of claims 1 to 3, wherein the hydrophobic thermoplastic polymer particles have a average particle size diameter in the range from 0.015 to 0.150 µm.

5. An imaging element according to any of claims 1 to 4, wherein the hydrophobic thermoplastic polymer particles are present in the image forming layer in an amount of at least 50 wt%.

6. An imaging element according to any of claims 1 to 5, wherein a hydrophilic polymer binder is present in said image forming layer or a layer adjacent thereto.

7. An imaging element according to any of claims 1 to 6, wherein the infrared absorbing compound is an anionic infrared cyanine dye absorbing infrared radiation in the wavelength range from 800 to 1100 nm and wherein the infrared absorbing compound is present in said image forming layer or in a layer adjacent thereto.

8. An imaging element according to any of claims 1 to 7, wherein the surface is a lithographic surface, present on a metal support, being a plate or a print cylinder.

9. A method for making a lithographic printing plate comprising the steps of:

-image-wise exposing to infrared light an imaging element according to any of the claims 1 to 8;

-developing the image-wise exposed imaging element by mounting it on a print cylinder of a printing press and applying an aqueous dampening liquid and/or ink to said imaging element while rotating said print cylinder.

10. A method for making a lithographic printing plate according to claim 9, wherein said imaging element is present on the press before starting image-wise exposing to infrared light an imaging element according to any of the claims 1 to 8.

11. Use of hydrophobic polymer particles containing more than 0.1 % of nitrogen in a coating of a heat sensitive imaging element according to any of claims 1 to 8.

12. Use of hydrophobic polymer particles containing more than 0.1 % of nitrogen in an image-forming layer of a heat sensitive imaging element according to any of claims 1 to 8.

13. Use of hydrophobic polymer particles containing structural chemical groups selected from the group consisting of amide, urethane, acrylonitrile, vinylcarbazole, methacrylonitrile, crotononitrile, vinylidene cyanide, isocytosine, pyrrolidone,

piperazine, cyanomethyl, cyanoethyl, cyanopropyl, cyanoaryl, cyanoacrylate, primary amines, mono- or di- n-alkyl substituted amines, urea, imide, imine, triazine, sulfonamide, onium, melamine, pyrimidine, ureido-pyrimidone, pyridine, barbiturate, isocyanurate or imidazole in a coating of a printing plate.

[ABSTRACT]

TITLE

NEGATIVE WORKING THERMAL PLATE FOR ON-PRESS DEVELOPMENT

A heat sensitive imaging element has been disclosed, said imaging heat sensitive imaging element comprising, on a lithographic base with a hydrophilic surface thereupon, an image-forming layer including hydrophobic thermoplastic polymer particles and a hydrophilic polymer binder, and, optionally, an infrared absorbing compound, characterized in that said hydrophobic polymer particles are containing structural chemical groups selected from the group consisting of amide, urethane, methacrylonitrile, crotononitrile, vinylidene cyanide, isocytosine, pyrrolidone, piperazine, cyanomethyl, cyanoethyl, cyanopropyl, cyanoaryl, cyanoacrylate, primary amines, mono- or di- n-alkyl substituted amines, urea, imide, imine, triazine, sulfonamide, onium, melamine, pyrimidine, ureido-pyrimidone, pyridine, barbiturate, isocyanurate or imidazole. Moreover a method for making a lithographic printing plate has been given, said method comprising the steps of image-wise exposing to infrared light an imaging element as disclosed, followed by developing the image-wise exposed imaging element by mounting it on a print cylinder of a printing press and applying an aqueous dampening liquid and/or ink to said imaging element while rotating said print cylinder.

Within the particular object of improving solvent resistance and/or improving run length use of hydrophobic polymer particles containing more than 0.1 % of nitrogen in a coating of a printing plate, and, more particularly in an image-forming layer of a heat sensitive imaging element has been disclosed.

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